

Photolysis of Diuron

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Abstract: The major photoproducts observed in the photolysis of diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] (**2**) in aqueous solution resulted from a heterolytic substitution of chlorine by OH (photohydrolysis). A wavelength effect was observed: at 254 nm the formation of 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea (**3**) accounted for more than 90% of the conversion, whereas when the solution was irradiated in 'black light' (85% of photons emitted at 365 nm, about 7% at 334 nm), the major photoproduct was 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea (**4**). The presence of methanol favoured the photoreduction into 3-(3-chlorophenyl)-1,1-dimethylurea (**5**).

Completely different reactions were observed when **2** was irradiated in dry aerobic conditions on silica. They resulted from elimination or oxidation of methyl groups. The main photoproducts initially formed were 3-(3,4-dichlorophenyl)-1-methyl urea (**6**) and 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (**7**). In the second stage (**6**) was transformed into (3,4-dichlorophenyl)-urea (**8**) and 3-(3,4-dichlorophenyl)-1-formylurea (**9**); some other minor products such as monuron (**1**) were also identified. The formation rate of **6** and **7** was much slower on clay (montmorillonite or kaolin) than on silica.

In contrast with products **6** and **8**, the formation of **7** and **9** needed the presence of oxygen: they did not appear when diuron was irradiated in deoxygenated C₂Cl₃F₃. It can be concluded that the photolysis of diuron is highly dependent on the conditions of irradiation.

Key words: diuron, dichlorophenylurea, photolysis, phototransformation, wavelength effect

1 INTRODUCTION

Halogenophenylureas form one of the main groups of herbicides used for more than 40 years. They absorb sunlight and they can be photochemically transformed in the environment either dissolved in water or dispersed on inorganic or organic supports.

The photodegradation of these compounds was observed in the early sixties.^{1,2} Some years later photoproducts of monuron^{3–8} and diuron^{9,10} were identified in aqueous solutions irradiated in UV light. The study of monuron was much more detailed than that of

diuron, especially by Tanaka *et al.*^{5–9} In some cases methanol¹⁰ or surfactants^{6,8} were added to the solution to increase the solubility. Mazzochi and Rao observed the photolysis of monuron in pure methanol.¹¹

The photoproducts of monuron identified by Crosby and Tang⁴ in aerobic dilute aqueous solution exposed to polychromatic light did not involve the elimination of the chlorine atom. They observed the formation of 4-chloroaniline, 4-chloroformanilide, 4,4'-dichloro-carbanilide and products resulting from hydroxylation of the ring, from demethylation or from oxidation of methyl groups. Tanaka *et al.*⁵ obtained the same products plus several dimers and the hydroxylated product resulting from dechlorination. The presence of a surfactant ('Triton' X or 'Tergitol' TMN) increased the rate of monuron degradation, eliminated ring hydroxylation

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and enhanced the reductive dechlorination.⁶ The formation of biphenyl derivatives was also observed with monuron,^{7,8} and a radical mechanism was proposed. In methanolic solution monuron was found to react cleanly and form the dechlorinated herbicide fenuron.¹¹

Tanaka *et al.*⁹ also compared the photo-transformation of diuron in natural sunlight and with UV lamps. In both cases the main products identified were 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea (**3**) and 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea (**4**) in the approximate ratio 2:1. This ratio was a little lower in sunlight than with UV lamps. Product **3** accounted for 10–20% of the converted substrate according to the conditions. Minor but not negligible products resulted from demethylation and oxidation of methyl groups. Several chlorobiphenyl derivatives were also formed and more than 20% of products stayed unidentified and were classified as 'unknown polar products'.

It was reported by Durand *et al.*¹⁰ that, in the presence of a few percent of methanol, the main photoreaction of diuron was photoreduction into monuron, this reaction being slowed down by the presence of salts (sea water).

Nothing has been reported to our knowledge on the kinetics of formation of photoproducts nor about the photochemical behaviour of chlorophenylureas adsorbed on inorganic supports, although herbicides may be transformed on the surface of soil exposed to sunlight.

The aim of the present work was to compare the photochemical behaviour of diuron in two typical conditions representative of the environment: aqueous solution and dispersion on inorganic supports such as silica and clays. The study of the influence of the irradiation wavelength is useful to know if irradiations with UV lamps have the same effect as irradiation in sunlight. Experimental results obtained in this area are somewhat surprising. Another important point is the kinetics of formation of the main products to determine what products may accumulate and to understand the mechanism of the reaction.

The kinetics, the influence of wavelength and of the presence of organic matter in the aqueous solution may explain why some differences have been observed in the photochemical behaviour of chlorophenylureas.

2 MATERIALS AND METHODS

2.1 Chemicals

The structures of the chemicals studied are given in Fig. 1.

Diuron (**2**) was provided by Rhône-Poulenc Agrochimie. Its purity was higher than 99%, most probably

higher than 99.9% since only traces of impurities were detected by HPLC with UV detection. [¹H]NMR in deuteromethanol and deuteriochloroform (ref. chloroform at 7.27 ppm): 7.62 (d) (1H); 7.31 (d) (1H); 7.22 (dd) (1H); 6.42 (s) (1H); 3.03 (s) (3H). Coupling constants: H₂–H₆: 2.5 Hz, H₅–H₆: 8.6 Hz.

Monuron (**1**) 98% was purchased from Chem. Service, 3,4-dichlorophenylisocyanate 99% (**11**) from Aldrich and 3,4-dichloroaniline ≥ 97% (**12**) from Fluka. 1,1,2-Trichlorotrifluoroethane 99% used as solvent in some experiments was from Janssen.

Sand Fontainebleau from Prolabo (Rhône-Poulenc), particle size 150–200 μm, Montmorillonite Fluka, Kaolin Fluka and Iron III oxide Aldrich were used as supports. The sand was washed before use to eliminate traces of organic matter first with 3 M hydrochloric acid, then with water, with 0.1 M sodium hydrogen carbonate and finally with water until stabilisation of pH. It was then dried during several hours at 500°C. A part of this sand was ground and particles of size less than 50 μm were used in some experiments.

Compounds **4**, **6**, **7** were synthesized in house in the laboratory Synthèse et Etude de Systèmes à Intérêt Biologique.

2.1.1 Synthesis of 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea (**4**)

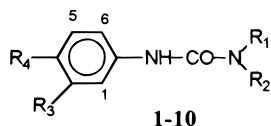
Compound **4** was obtained from 3-chloro-4-hydroxyaniline and carbamoyl chloride.

2.1.2 Synthesis of 3-(3,4-dichlorophenyl)-1-methylurea (**6**)

Compound **6** was prepared from 3,4-dichlorophenylisocyanate and dimethylamine according to the method described by Crosby and Tang.⁴ [¹H]NMR (400 MHz) in hexadeuteroacetone (ref. CD₃-CO-CHD₂ at 2.04 ppm): 8.15 (s) (1H); 7.89 (d) (1H); 7.33 (d) (1H); 7.27 (dd) (1H); 5.70 (s) (1H); 2.70 (d) (3H).

2.1.3 Synthesis of 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (**7**)

A similar method was used to obtain **7** from 3,4-dichlorophenylisocyanate and *N*-formylamine. [¹H]NMR (400 MHz) in deuteromethanol containing small amount of water (ref. CD₂HOD 3.50 ppm): 8.27 (s) (≈ 1/2H); 7.91 (d) (1H); 7.52 (d) (1H); 7.41 (dd) (1H); 2.93 (s) (3H). Minor broad signals were observed at 9.38 and 8.82 ppm. In dry methanol the signal at 8.27 ppm did not appear and peaks at 9.38 and 8.82 ppm correspond to around 3/5 H and 2/5 H. They are attributed to CHO. Aromatic proton H₂ is located at 8.0–8.1 ppm (double peak), aromatic protons H₅ and H₆ at 7.65 ppm without coupling and methyl at 3.40–3.45 ppm. This unexpected phenomenon, which was also observed with dry acetone, is not the subject of the present work.



	R ₁	R ₂	R ₃	R ₄
1 (monuron)	CH ₃	CH ₃	H	Cl
2 diuron	CH ₃	CH ₃	Cl	Cl
3	CH ₃	CH ₃	OH	Cl
4	CH ₃	CH ₃	Cl	OH
5	CH ₃	CH ₃	Cl	H
6	H	CH ₃	Cl	Cl
7	CHO	CH ₃	Cl	Cl
8	H	H	Cl	Cl
9	H	CHO	Cl	Cl
10	CH ₃	CH ₃	OH	OH

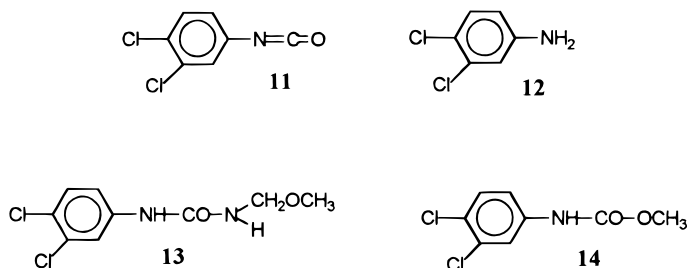


Fig. 1. Structures of compounds studied.

2.2 Irradiation

Solutions were irradiated in various conditions:

- at 254 nm in a quartz reactor with germicide lamps;
- at 296 nm with a monochromator (Bausch and Lomb) equipped with a high pressure mercury lamp;
- in the range 290–350 nm with fluorescent lamps (Duke Sunlamp GL 20) having maximum emission at 310 nm;
- with ‘black light’ lamps emitting 85% of photons at 365 nm and about 7% at 334 nm; and
- at $\lambda > 300$ nm with the rotating round-bottom flask described below for irradiation of powders.

A special procedure was used for the irradiation of diuron dispersed on inorganic powders. First diuron was dissolved in diethyl ether. This solution was mixed with dry support suspended in diethyl ether by magnetic stirring. After evaporation of the bulk of the solvent, the remainder was removed by keeping under vacuum overnight.

The substrate dispersed on inorganic support was irradiated in the device represented in Fig. 2. It consists

of a Pyrex round-bottom flask rotating around the horizontal axis, cooled with a water bath and irradiated with two medium-pressure mercury lamps (Mazda MA 400 W). In these lamps, the central mercury arc is surrounded by a bulb which cuts off wavelengths shorter than about 310 nm. In most of experiments these lamps were used after removing the bulb to increase the light

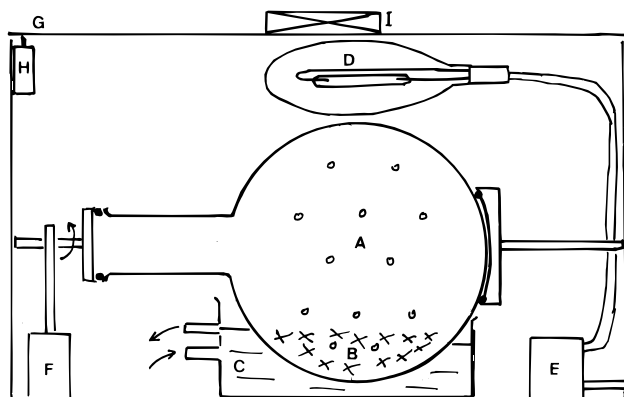


Fig. 2. Device used for irradiation of solids or aqueous suspensions. A: Round-bottom flask (4 l); B: solid to be irradiated; C: water bath; D: medium pressure mercury lamp; E: power supply; F: motor; G: opening cover; H: switch for security; I: fan for lamp cooling and elimination of ozone.

intensity in the range 290–310 nm. The flask was equipped with internal spikes in order to obtain a good mixing of the powder. The same device was used for dry powders, solutions, slurries or suspensions. Three different methods were used to extract organic compounds after irradiation.

For separation of products formed on sand, the irradiated sample was extracted four times in a glass filter with 20 ml of hexane and then four times with methanol. After evaporation of hexane the dried substance was dissolved in methanol, and water was added shortly before HPLC separation to prevent peaks broadening. The extract in methanol was concentrated and an equal volume of water was added before HPLC separation.

For kinetic measurements samples were extracted with ether. After evaporation the dry extract was dissolved in a known volume (10 ml) of methanol + water (5 + 5 by volume).

With clays and iron (III) oxide, which may diffuse through the glass filter, 25 g of the irradiated solid was placed into the bottom of the special extraction device shown in Fig. 3 with 150 ml of water. Ether condensed in the upper part dropped into the funnel, diffused through the glass filter and extracted organic products

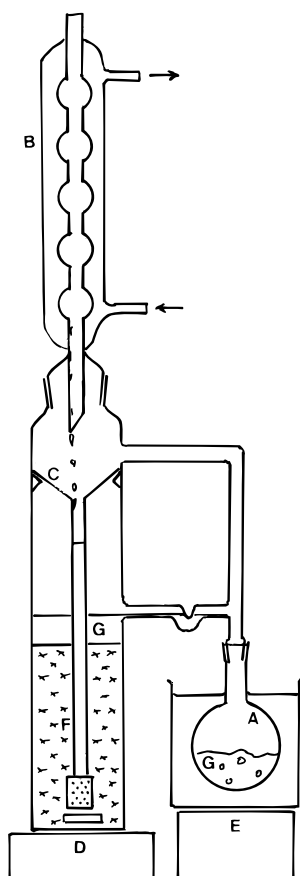


Fig. 3. Device used for the extraction of clays. A: Boiler; B: condenser; C: funnel; D: magnetic stirrer; E: heater; F: solid to be extracted in aqueous suspension; G: ether.

from the water phase, so that they concentrated in the round-bottom flask. This procedure took about 24 h for each sample. After evaporation of ether, products were dissolved in methanol + water (52 + 48 by volume) for HPLC analysis.

2.3 HPLC analysis

UV spectra were recorded on a Cary 3 spectrophotometer (Varian) in a 1-cm quartz cuvette. The irradiated solutions were analysed by HPLC on a 250×4.6 mm or 125×4.6 mm C_{18} column using methanol + water (usually 52 + 48 or 70 + 30 by volume) as eluent. Several HPLC were used: Beckman with UV detector, Waters with a photodiode array detector and Merck with both UV and fluorescence detectors.

Isolated products were identified by $[^1H]NMR$ at 400 MHz on a Bruker AC 400 with the collaboration of Centre Régional de Mesures Physiques and by mass spectrometry (70 E type EB Fison), in Service Central d'Analyses of Centre National de la Recherche Scientifique (CNRS). High resolution mass determination on VG ZAB2-SEQ was used for the identification of some products.

3 RESULTS

3.1 UV absorption

The solubility of diuron in water was evaluated at about 42 mg litre^{-1} i.e. $1.9 \times 10^{-4} \text{ M}$ by comparing the UV spectrum of a saturated solution to the spectrum of a solution of known concentration in water + methanol (80 + 20 by volume).

The UV spectrum of diuron in aqueous solution is given in Fig. 4. The two main absorption bands are located at 247 and 284 nm with molar extinction coefficients evaluated at $17\,600 (\pm 300)$ and 1330

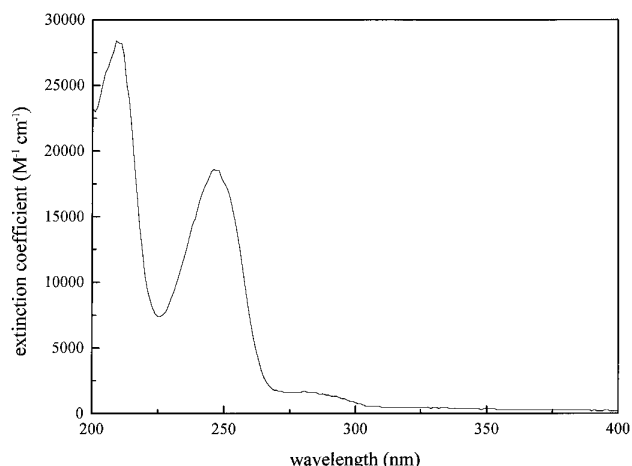


Fig. 4. UV spectrum of an aqueous solution of diuron.

(± 50) $\text{cm}^{-1} \text{M}^{-1}$ respectively. The absorption is very low but not completely negligible between 320 and 370 nm.

Trichlorotrifluoroethane ($\text{C}_2\text{Cl}_3\text{F}_3$) was used as the solvent in some experiments in order to determine the influence of oxygen in an aprotic solvent. The UV spectrum of diuron is not obviously different in this solvent. The maxima are located at 245 and 288 nm and the molar extinction coefficients are about 10% higher.

3.2 Irradiation of aqueous solutions

3.2.1 In UV light

When an air-saturated solution ($1.3 \times 10^{-4} \text{ M}$) was irradiated at 254 nm, the UV absorption increased in the range 270–310 nm and decreased between 240 and 260 nm but no typical new band was observed. On the HPLC chromatogram of the irradiated solution obtained with methanol + water (52 + 48 by volume) as eluent (Fig. 5(a)), two products P_1 and P_2 could be detected. Their UV spectra obtained with the photodiode array detector were slightly different from that of diuron. The main band was just a little blue shifted (about 8 nm for P_1 and 2 nm for P_2). Both products were isolated and found to have similar mass spectra, the parent peak being located at $m/e = 214$. This value is consistent with the formula $\text{C}_9\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$. From the NMR spectra P_1 was identified as compound **4** and P_2 as **3**.

NMR shifts in deuteriochloroform (ref. CHCl_3 7.27 ppm) were:

P_1 : 7.55 (d) (1H), 7.06 (dd) (1H), 6.93 (d) (1H), 6.3 (s) (1H), 3.00 (s) (6H);

P_2 : 7.20 (d) (1H), 7.19 (d) (1H), 6.90 (dd) (1H), 6.3 (s) (1H), 3.00 (s) (6H).

Compound **4** was synthesized as indicated in Section 2.1.1 in order to calibrate HPLC chromatograms. It

was deduced that P_2 initially accounted for about 95% of the diuron transformed. The formation of **4** was estimated to be about 1/20 of **3** assuming that **3** and **4** have the same absorption coefficient at the detection wavelength (250 nm). The kinetics of formation of **3** and **4** are given in Fig. 6. During the first stage the reaction is almost specific.

The quantum yield of the phototransformation of diuron was evaluated at 0.02 using ferrioxalate as the actinometer.

The same results were obtained with a solution deoxygenated by argon bubbling. It was deduced that oxygen is not involved in the reaction. It was also observed that chlorine ions (solution saturated with sodium chloride) have almost no influence on the formation of **3** and **4**.

The wavelength 254 nm corresponds to the second absorption band of diuron and it is not in the range of tropospheric sunlight. In order to control the influence of wavelength, solutions were monochromatically irradiated at 296 nm and with 'black light' lamps (85% of the emission located on the 365 nm line of mercury and about 7% at 334 nm). Polychromatic light emitted by a medium pressure mercury lamp filtered by Pyrex was also used. In all cases products **3** and **4** were the main photoproducts but they were not formed in the same ratio. With 'black light' the ratio **4/3** was about 10 (Fig. 6(b)). In contrast this ratio was about 1/20 when solutions were irradiated at 254 nm (Fig. 6(a)). This wavelength effect cannot be attributed to the photolysis of **3** at long wavelengths since this photolysis might hinder the accumulation of **3**. Actually it was observed that both products **3** and **4** linearly accumulated in the first stage of the reaction. It cannot be attributed to the excitation of the absorption band centred at 247 nm and near 284 nm respectively because the ratio **4/3** obtained at 296 nm was about 1/10 and about 1/1 with natural daylight.

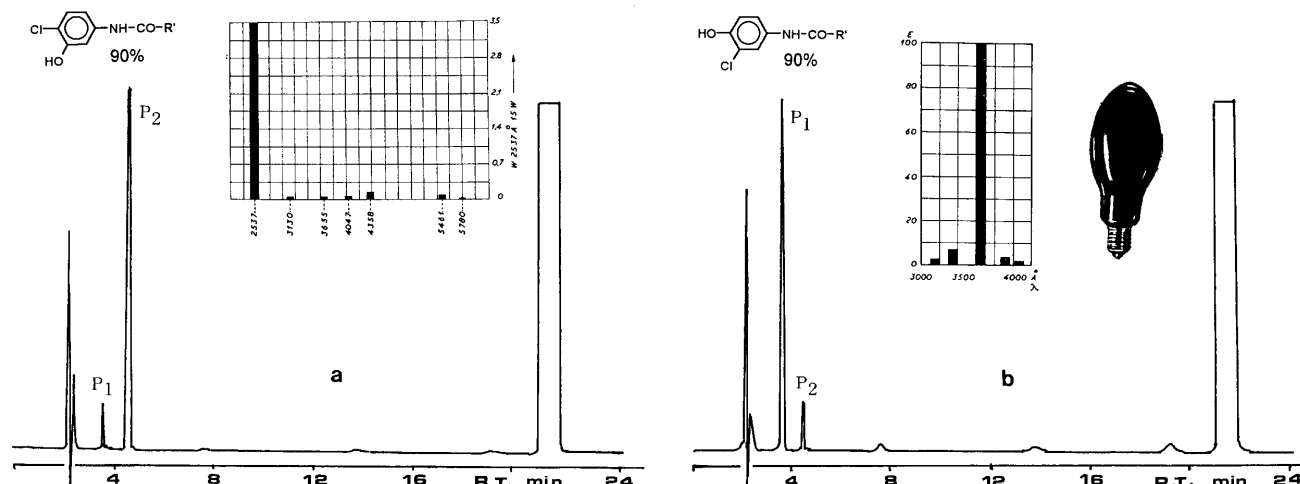


Fig. 5. HPLC chromatogram of an aqueous solution of diuron ($1.3 \times 10^{-3} \text{ M}$) (a) irradiated at 254 nm and (b) in 'black light'. Detection at 250 nm. Eluent: methanol + water (52 + 48 by volume). $\text{R}' = -\text{N}(\text{CH}_3)_2$.

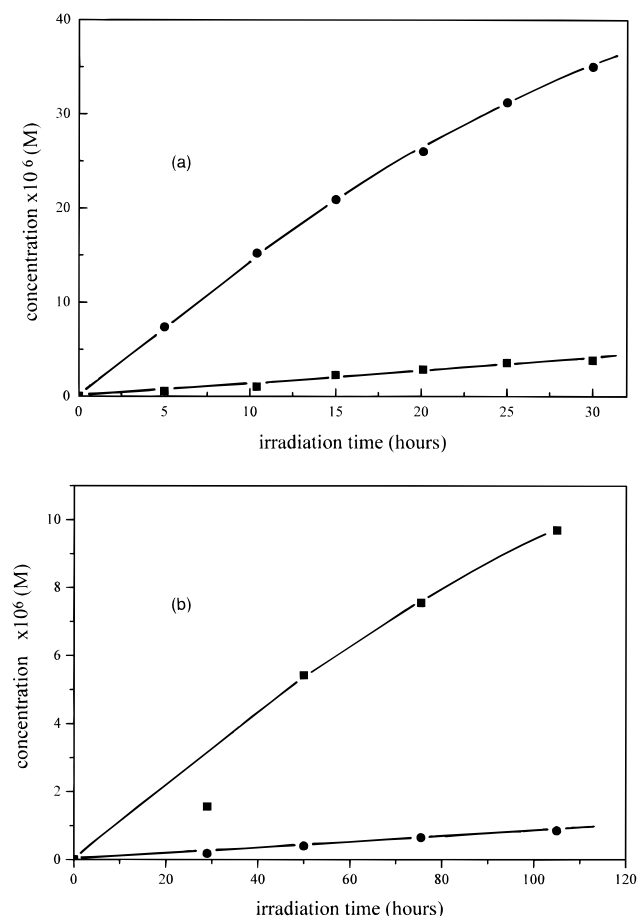


Fig. 6. Kinetics of formation of products (■) P_1 (4) and (●) P_2 (3) in the phototransformation of diuron in aqueous solution (1.3×10^{-3} M) (a) irradiated at 254 nm (b) irradiated in 'black light'.

A study of this unexpected phenomenon is in progress.

3.2.2 Solar irradiation

A 10^{-4} M solution of diuron was exposed to solar irradiation in a Pyrex cylindrical container for about five months during the winter season in Clermont-Ferrand (latitude 46°N ; 400 m above sea level). The rate constant of apparent first-order reaction was $c. 3 \times 10^{-3} \text{ day}^{-1}$ (Fig. 7). It can also be seen on Fig. 7 that 3 and 4 were formed as primary products and 6 as a secondary product. Another product of low retention time was tentatively attributed to 10.

3.3 Irradiation on sand in dry conditions

Diuron was dispersed on the following inorganic supports and irradiated in the special device described in Section 2.2:

- sand Fontainebleau (pure silica) particle size 150–200 μm ;

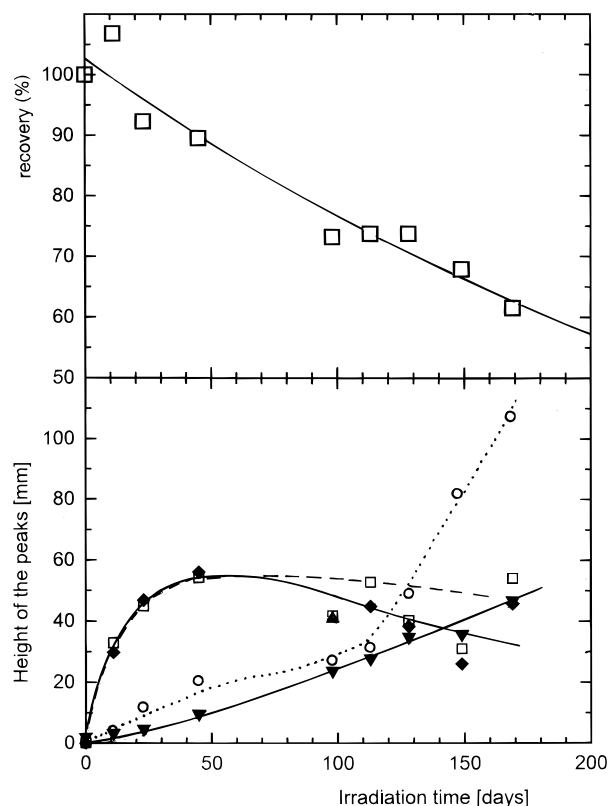


Fig. 7. Kinetics of photolysis of diuron 10^{-4} M in aqueous solution exposed to solar irradiation (November–March). (◆) 3, (□) 4, (▼) 6, (○) 10.

- sand Fontainebleau ground and sieved to reduce particle size to below 50 μm ; and
- two clays: montmorillonite and kaolin.
- iron(III) oxide

Most of experiments were carried out with natural sand; the clays and ground sand were used to study the influence of support and specific area respectively.

3.3.1 Identification of products

Diuron (100 mg) was deposited on sand (200 g) and irradiated in the device represented on Fig. 2. Every day an aliquot of sand (250 mg) was separated for analytical control. The experiment was stopped after 10 days. Organic components were extracted first with hexane and then with methanol. The chromatograms of these extracts are given in Fig. 8 and 9. The main photoproducts D_1 – D_6 were isolated and analysed by MS and $[^1\text{H}]\text{NMR}$ (except for D_6 , the amount isolated being too small). Results are summarised in Tables 1 and 2.

The NMR spectrum of D_5 is identical to that of product 7 when methanol contains traces of water.

Photoproducts were identified as: D_1 : monuron; D_2 : 8; D_3 : 6; D_4 : 9; D_5 : 7 and D_6 : 13 (tentatively).

Product 13 is an isomer of linuron [3-(3,4-dichlorophenyl)-1-methyl-1-methoxyurea]. It was shown that D_6 had not the same HPLC retention time as linuron, which is a commercial compound.

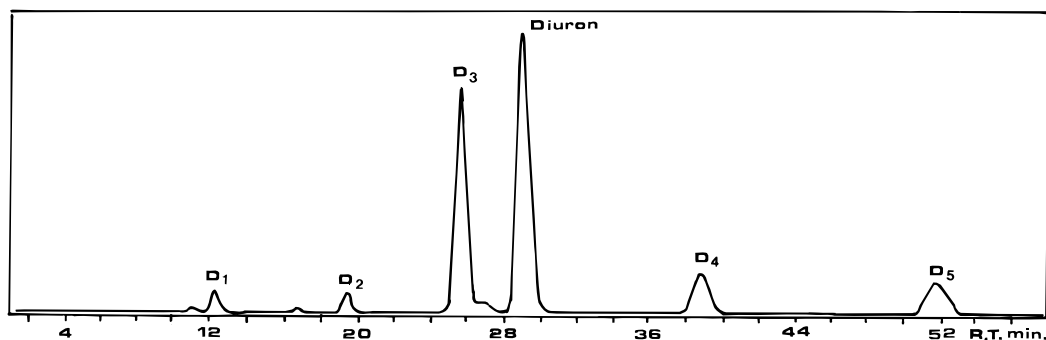


Fig. 8. HPLC chromatogram of the hexane extract of diuron irradiated on natural sand. HPLC conditions: column C_{18} 250×4 mm, detection $\lambda = 250$ nm, eluent methanol + water (13 + 12 volume). Identification: D_1 : monuron, D_2 : **8**, D_3 : **6**, D_4 : **9**, D_5 : **7**.

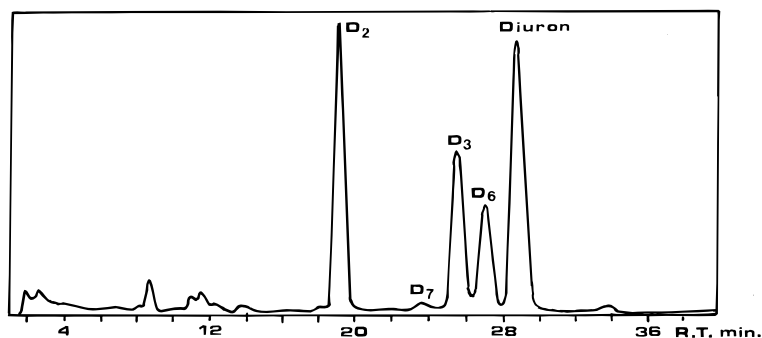


Fig. 9. HPLC chromatogram of the methanolic extract of diuron irradiated on natural sand. Same HPLC conditions as in Fig. 8. Identification: D_2 : **8**, D_3 : **6**, D_6 : **13**.

TABLE 1
MS Analyses of the Products Isolated in the Photolysis of Diuron on Natural Sand (Fontainebleau)

	<i>m/e</i> low resolution parent peak and fragments	<i>m/e</i> high resol.	Formula
D_1	198 (1Cl)		$C_9H_{11}ClN_2O$
D_2	204 (2Cl)		$C_7H_6Cl_2N_2O$
D_3	218 (2Cl)	218·0013	$C_9H_8Cl_2N_2O$
D_4	232 (2Cl)		$C_8H_6Cl_2N_2O_2$
D_5	216 (2Cl), 187 (2Cl), 161 (2Cl)	245·9957	$C_9H_8Cl_2N_2O_2$
D_6	248 (2Cl), 216 (2Cl), 187 (2Cl), 161 (2Cl)	248·0115	$C_9H_{10}Cl_2N_2O_2$

TABLE 2
[1H]NMR Spectra in Deuteriomethanol of the Products Isolated in the Photolysis of Diuron on Natural Sand. Shifts (ppm) ref. CD_2HOD 3·50 ppm

D_1	7·55 (d) (2H); 7·42 (d) (2H)	3·20 (s) (6H)
D_2	7·93 (d) (1H); 7·55 (d) (1H); 7·42 (dd) (1H)	
D_3	7·91 (d) (1H); 7·53 (d) (1H); 7·40 (dd) (1H); 2·95 (s) (3H)	
D_4^a	8·27 (s) ($\approx 1\cdot2H$); 7·92 (d) (1H); 7·55 (d) (1H); 7·42 (dd) (1H)	
D_5^b	9·38 (s) ($\approx 1H$); 8·02 (s) ($\approx 1H$); 8·10 (s) ($\approx 1H$); 7·63 (s) ($\approx 2H$); 3·40 (s) ($\approx 3H$); 3·44 (s) ($\approx 3H$)	
	minor peaks at 7·9 (d); 7·53 (d); 7·41 (dd); 2·94 (s)	

^a Sample containing a small amount of water.

^b The NMR spectrum of D_5 is identical to that of product **7** when methanol contains traces of water.

3.3.2 Kinetic study

For the kinetic study, 2 mg of diuron was deposited on 400 g of sand and samples of 50 g were irradiated with the device shown in Fig. 2 equipped with lamps without bulb ($\lambda > 300$ nm). The kinetics of transformation of diuron and the formation of the main photoproducts can be seen in Figs 10 and 12 for natural sand (150–200 μm) and ground sand (< 50 μm) respectively. Monuron (1) and compounds 6 and 7 have kinetics of primary products, 8 and 9 kinetics of secondary products. Other experimental evidence is that the transformation is slower on ground sand than on natural sand. Two explanations may be suggested (i): Some ground sand stays electrostatically fixed on the rotating round-bottom flask and has a screening effect; (ii): ground sand is more light-diffusing.

3.4 Irradiation on clays and iron (III) oxide

Diuron was deposited on kaolin, montmorillonite and iron (III) oxide in the same proportion as on sand. However, it was not possible to extract the solution directly on a glass filter because the support diffused through the filter. Irradiated supports were extracted with ether as described in Section 2.2 using the device presented in Fig. 3.

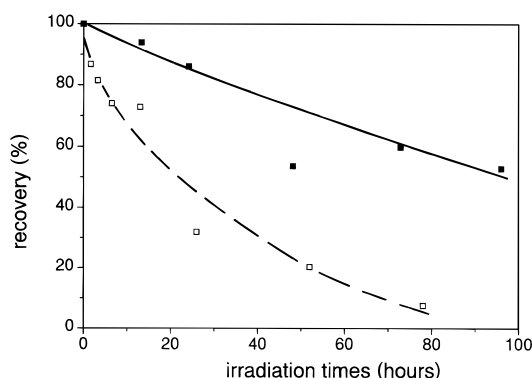


Fig. 10. Kinetics of photolysis of diuron (0.25 mg/50 g) on (□) natural sand (150–200 μm), and (■) ground sand (≤ 50 μm).

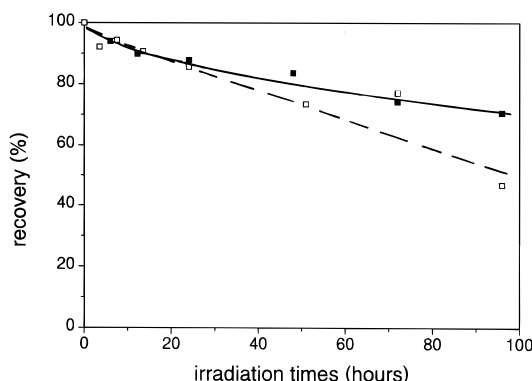


Fig. 11. Kinetics of photolysis of diuron on (■) kaolin and (□) montmorillonite (0.25 mg/50 g).

On iron (III) oxide the transformation was extremely slow, just detectable after 100 h. Formation of 6 was observed.

On kaolin and montmorillonite the transformation was slower than on natural sand as shown in Figs 10–12. The formation of 6 and 7 was observed but two other unidentified products characterised by short HPLC retention times were also formed. The difference of kinetics between iron (III) oxide and sand can be attributed to the absorption of light by iron (III) oxide which introduces a strong screening effect. The difference between silica and clays is not so clear. The screening effect plays probably a minor role: The rate is a little slower on montmorillonite than on kaolin which contains more iron. Diffusing properties and electrostatic retention on the reactor may also have an influence. Actually it was experimentally proven with a spectrophotometer equipped with an integration sphere that aqueous suspensions of ground sand are less light-diffusing than suspensions of clays in the same conditions.¹²

3.5 Irradiation of diuron in aqueous suspensions of sand

Three experiments were performed with an aqueous solution of diuron (5×10^{-5} M) to which natural or ground sand was added.

1. Natural sand (50 g) was added to 50 ml of solution and irradiated at $\lambda > 310$ nm (lamp with bulb);
2. the same mixture was irradiated at $\lambda > 300$ nm (lamp without bulb);
3. ground sand (50 g) was added to 50 ml of solution and irradiated at $\lambda > 310$ nm.

It was observed that, in the aqueous suspension of natural sand, the phototransformation proceeded, as in water, predominantly through the two primary products 3 and 4.

The reaction rate of disappearance of diuron was slower by approximately one order of magnitude when

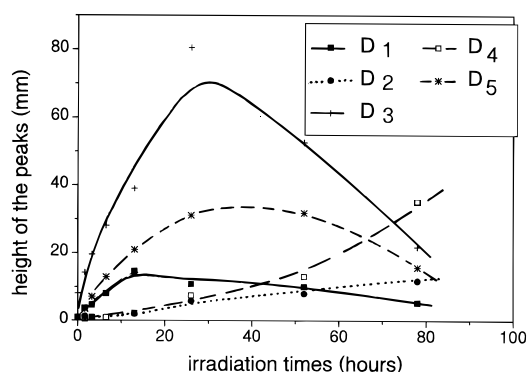


Fig. 12. Kinetics of formation of the main products of the phototransformation of diuron on natural sand.

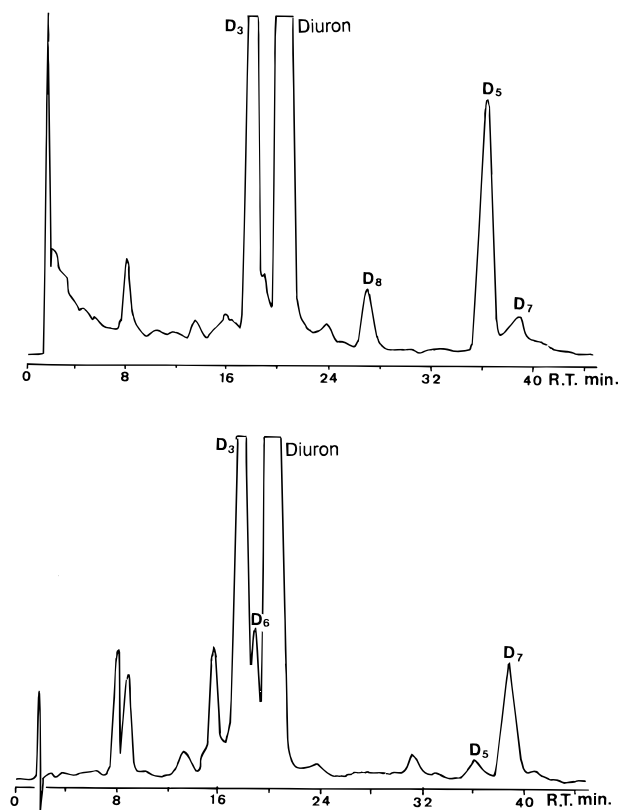


Fig. 13. HPLC chromatogram of the photoproducts of diuron irradiated at 313 nm in $C_2Cl_3F_3$. Detection 250 nm, eluent methanol + water (13 + 12 by volume). A: air-saturated solution B: degassed solution. Identification: D_3 : **6**, D_5 : **7**, D_6 : **13**, D_7 : **14**, D_8 : $C_8H_8Cl_2N_2O$.

the light was filtered by the bulb of lamps. The proportion between **3** and **4** depended on this filtering effect, but not markedly so. With a dense aqueous suspension of ground sand only very small amounts of intermediates could be detected in the aqueous phase because of their adsorption on the sand.

3.6 Preparative irradiation of diuron in 1,1,2-trichloro-1,2,2-trifluoroethane and in methanol

An aprotic solvent, 1,1,2-trichloro-1,2,2-trifluoroethane was used to study the influence of oxygen on the phototransformation of diuron in the absence of water. Solutions of about 10^{-3} M were irradiated at 313 nm both in the presence and in the absence of air. It appears on the chromatograms of Fig. 13 that the main difference is that product D_5 is much reduced and new photoproducts are formed. Product D_7 was isolated and analysed. From the mass spectrum ($m/e = 218.9856$ fragments at 187 and 160) and its NMR spectrum in deuteriochloroform (ref. $CHCl_3$ at 7.27 ppm): 7.63 d (1H), 7.36 d (1H), 7.21 dd (1H), 6.6 s (1H), 3.8 s (3H), D_7 was identified as **14**. This product results from the methanolysis of dichloroisocyanate (**11**) during HPLC.

Another product (D_8) was isolated and analysed by mass spectrometry ($m/e = 218.0013$ fragments at 187, 161, 124). It is dichlorinated and the most probable formula deduced from the high resolved mass is $C_8H_8Cl_2N_2O$. It is probably a mixture of several isomers since the ratio of fragments $m/e = 187$ and $m/e = 161$ is not constant during the recording of the mass spectrum.

When solutions of diuron were irradiated in the presence of a few percent of methanol, a new product was observed, its HPLC retention time being intermediate between the retention time of diuron and that of hydroxylated derivatives. This compound is the major product when diuron is irradiated in pure methanol. It was isolated and from its NMR spectrum in deuterated acetone it was unambiguously identified with **5**.¹³

4 DISCUSSION AND MECHANISMS

The formation of hydroxychloroderivatives is a typical reaction in aqueous solutions. Chlorine is converted into chloride ion and the reaction is almost specific as was observed with chlorobenzene, 3-chlorophenol and 3,4-dichlorophenol.^{14–16} It is attributed to a heterolytic photohydrolysis. Thus the formation of product **3** from diuron at short wavelengths can be explained by the excitation of the aromatic ring. (Fig. 14(a)).

The formation of isomer **4** at long wavelengths is more surprising since such a wavelength effect was not observed with 3,4-dichlorophenol which yields 4-chlororesorcinol as the major photoproduct whatever the wavelength. It can be related to the presence of a carbonyl group. The study of the mechanism involved is still in progress.

The phototransformation of **3** and **4** in the second stage is expected to yield **10**.

In the presence of methanol the excited state of diuron can be reduced into **5**.

The formation of **6** is not oxygen-dependent since it was observed both in aerobic conditions and in deoxygenated $C_2Cl_3F_3$. The demethylation can be explained by the intermediate formation of a methylenolate which reacts with water during HPLC analysis after irradiation. (Fig. 14(b)).

In the presence of oxygen the oxidation of **2** into **7** competes with the formation of **6**. This oxidation is probably favoured by the possibility of an internal hydrogen bond in the excited state. (Fig. 14(c)).

A similar mechanism can explain the formation of **8** and **9** from **6** in the second stage of the reaction.

The formation of **14** in deoxygenated $C_2Cl_3F_3$ is attributed to the elimination of diethylamine. Dichloroisocyanate is formed but reacts with methanol during HPLC analysis (Fig. 14(d)).

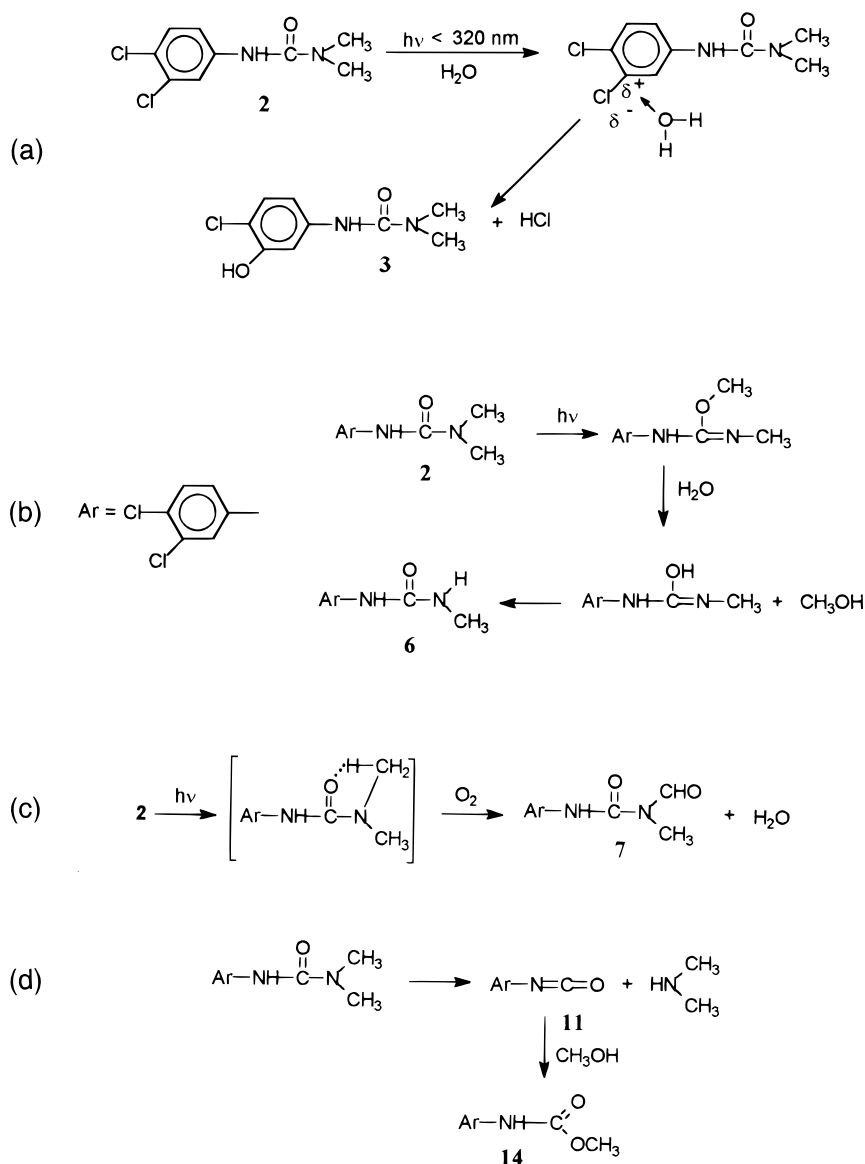


Fig. 14. Routes of formation of photoproducts of diuron.

5 CONCLUSIONS

The phototransformation of diuron is obviously different in pure water and under dry conditions. The formation of chlorohydroxyphenyldimethylurea, only observed in aqueous solution, does not depend on the presence of oxygen. It results from a heterolytic photolysis. The wavelength effect may be related to the carbonyl group since it is not observed with 3,4-dichlorophenol. In the presence of a few percent of methanol, a reduction into 3-(3-chlorophenyl)-1,1-dimethylurea occurs.

The main reactions observed by irradiating diuron dispersed on sand in aerobic conditions are the oxidation and the elimination of one or both methyl groups. The same products are formed on clays but the reactions are much slower. The demethylation can occur in

the absence of oxygen since it was also observed in deoxygenated $C_2Cl_3F_3$.

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